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Electronic states and nature of bonding in the molecule MoC by all electron *ab initio* calculations

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In the present work all electron *ab initio* multiconfiguration self-consistent-field (CASSCF) and multireference configuration interaction (MRCI) calculations have been carried out to determine the low-lying electronic states of the molecule MoC. The relativistic corrections for the one electron Darwin contact term and the relativistic mass-velocity correction have been determined in perturbation calculations. The electronic ground state is predicted as $^3\Sigma^-$. The spectroscopic constants for the $^3\Sigma^-$ electronic ground state and eight low-lying excited states have been derived by solving the Schrödinger equation for the nuclear motion numerically. Based on the results of the CASSCF calculations the $^3\Sigma^-$ ground state of MoC is separated from the excited states $^3\Delta$, $^5\Sigma^-$, $^1\Gamma$, $^1\Delta$, $^5\Pi$, $^1\Sigma^+$, and $^3\Pi$ by transition energies of 4500, 6178, 7207, 9312, 10 228, 11 639, and 16 864 cm^{-1} , respectively. The transition energy between the $^3\Sigma^-$ ground state and the $^3\Pi$ state as derived in the MRCI calculations is 15 484 cm^{-1} . For the $^3\Sigma^-$ ground state the equilibrium distance has been determined as 1.688 Å, and the vibrational frequency as 997 cm^{-1} . The chemical bond in the $^3\Sigma^-$ electronic ground state has triple bond character due to the formation of delocalized bonding π and σ orbitals. The chemical bond in the MoC molecule is polar with charge transfer from Mo to C, giving rise to a dipole moment of 6.15 D at 3.15 a.u. in the $^3\Sigma^-$ ground state.

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I. INTRODUCTION

With the present investigation of the MoC molecule we are continuing our systematic study of the electronic structure and nature of bonding in the diatomic transition metal carbides.¹⁻⁹

The only experimental result reported for the MoC molecule is its dissociation energy obtained from equilibrium mass spectrometric measurements¹⁰ as 114.2 ± 3.8 kcal/mol $= 4.95 \pm 0.16$ eV. Using the results of the present investigation the dissociation energy of MoC has been re-evaluated as 5.01 ± 0.13 eV.

In the present investigation we report results of *ab initio* calculations. The low-lying states of the MoC molecule have been studied by performing all electron *ab initio* calculations. The methods employed are Hartree-Fock (HF), and multiconfiguration self-consistent-field (MCSCF) calculations within the complete active space self-consistent-field approach (CASSCF). The HF calculations have been carried out in the Hartree-Fock-Roothaan formalism.¹¹ The program system MOLCAS, version 3¹² has been used for carrying out the CASSCF calculations. The relativistic effects on the low-lying electronic states have been considered by performing perturbation calculations to determine the one electron Darwin contact term and the relativistic mass-velocity correction. In addition, multireference configuration interaction calculations (MRCI) have been performed to investigate further the electronic ground state of the MoC molecule and also the lowest lying excited state that can be reached from the ground state by an allowed transition.

II. BASIS SETS AND HF CALCULATIONS ON MoC

The basis sets consisted of contracted Gaussian type functions. For the Mo atom we have used Huzinaga's (17s,11p,8d) basis set,¹³ but it has been extended by addition of two *p* functions with exponents 0.1496 and 0.0620. These functions are needed to represent the 5*p* orbitals. In addition, the most diffuse *s* functions have been contracted slightly by altering the exponents from 0.084 897 748 and 0.032 362 164 to 0.0945 and 0.0408, respectively. Finally an *f* polarization function with exponent 0.692 has been added. The primitive basis set (17s,13p,8d,1f) has been contracted to (10s,8p,5d,1f) using a segmented contraction scheme. In the contracted basis the 4*d* orbitals are represented by a triple zeta function while all other orbitals including the unoccupied 5*p* orbitals are represented by double zeta functions. For the C atom we have used Huzinaga's (10s,6p) basis,¹⁴ but it has been augmented by a *d* polarization function with exponent 0.75. The basis set for the C atom has been contracted to (4s,3p,1d) resulting in double zeta representation of the *s* functions, triple zeta representation of the 2*p* function, and a *d* polarization function.

The electronic ground term of the Mo atom is $^7S_g(4d)^5(5s)^1$ and that of the C atom is $^3P_g(2s)^2(2p)^2$. According to our previous work on other second series transition metal carbides, RhC (2,3), RuC (3,4), and PdC (1,3) we expected that the electronic structure of MoC can be rationalized in a molecular orbital picture. Thus, the interaction between the Mo $^7S_g(4d)^5(5s)^1$ and the C $^3P_g(2s)^2(2p)^2$ should give rise to the molecular

configurations $(2\delta)^2(5\pi)^3(10\sigma)^2(11\sigma)^2(12\sigma)^1$ and $(2\delta)^2(5\pi)^4(10\sigma)^2(11\sigma)^1(12\sigma)^1$, where the single occupied σ orbitals are either of the Mo orbitals, $4d\sigma$ or $5s$. However, the interaction could also result from Mo $^7S_g(4d)^5(5s)^1$ and C in the excited term $^5S_u(2s)^1(2p)^3$. The resulting molecular configuration would then be $(2\delta)^2(5\pi)^4(10\sigma)^2(11\sigma)^2$. This configuration could also result from the interaction between the ions, $\text{Mo}^+ ^6S_g(4d)^5$ and $\text{C}^- ^4S_u(2s)^2(2p)^3$. The formal bond order in the above-mentioned configurations is the largest in the configuration $(2\delta)^2(5\pi)^4(10\sigma)^2(11\sigma)^2$. This configuration can give rise to molecular states of the symmetries $^1\Sigma^+$, $^1\Gamma$, and $^3\Sigma^-$. Since the spins of the partly occupied 2δ orbitals are anti parallel coupled in the singlet states, the most likely ground-state candidate for the MoC molecule is $^3\Sigma^-$. In this state the two electrons in the 2δ orbitals have parallel coupled spins.

In order to get a first impression of the electronic states of the MoC molecule, Hartree-Fock calculations have been performed on the above-mentioned $^3\Sigma^-$ state. The Mulliken population analyses of this state shows a charge transfer of $0.43e$ from Mo to C at 3.1 a.u. Furthermore, the 10σ orbital is essentially a bonding combination of the C $2s$ orbital and a Mo sd -hybrid orbital. Likewise the 11σ orbital is a bonding combination of a C sp -hybrid and the Mo $4d\pi$ orbitals. The 5π orbital is the bonding combination of the C $2p\pi$ and the Mo $4d\pi$ orbitals. Thus, the chemical bond in the $^3\Sigma^-$ state of the MoC molecule as described in the HF approximation is formally a quadruple bond. In spite of this, the Hartree-Fock calculations on the $^3\Sigma^-$ state revealed that the MoC molecule is bound by only 0.10 eV relative to the free HF atoms.

It is well known that HF calculations do not give reliable results for molecules containing transition metal atoms. In the case of the MoC molecule, this is confirmed with the present calculations, since the experimentally determined dissociation energy of the MoC molecule amounts to 5.01 ± 0.13 eV as compared to the calculated value of 0.10 eV. In order to investigate the electronic structure of the MoC molecule further, MCSCF calculations within the CASSCF framework have been performed on the above mentioned $^3\Sigma^-$ state of MoC as well as on states of other symmetries.

III. RESULTS OF CASSCF CALCULATIONS

In the CASSCF calculations the core orbitals, i.e., the $1s$, $2s$, $3s$, $4s$, $2p$, $3p$, $4p$, and $3d$ of Mo and the $1s$ orbital of C, were kept fully occupied, while the valence orbitals $5s$ and $4d$ of Mo and $2s$ and $2p$ of C, have been included in the active space. The CASSCF calculations have been performed in the subgroup C_{2v} of the full symmetry group $C_{\infty v}$ of the MoC molecule. The calculations have been carried out for singlet, triplet, and quintet states. The number of configurations included in the CASSCF calculations reached 4984 for the singlet states, 7476 for the triplet states, and 3135 for the quintet states.

The relativistic effects have been considered by carrying out perturbation calculations to derive values for the one

Energy (a.u.) +4012a.u.

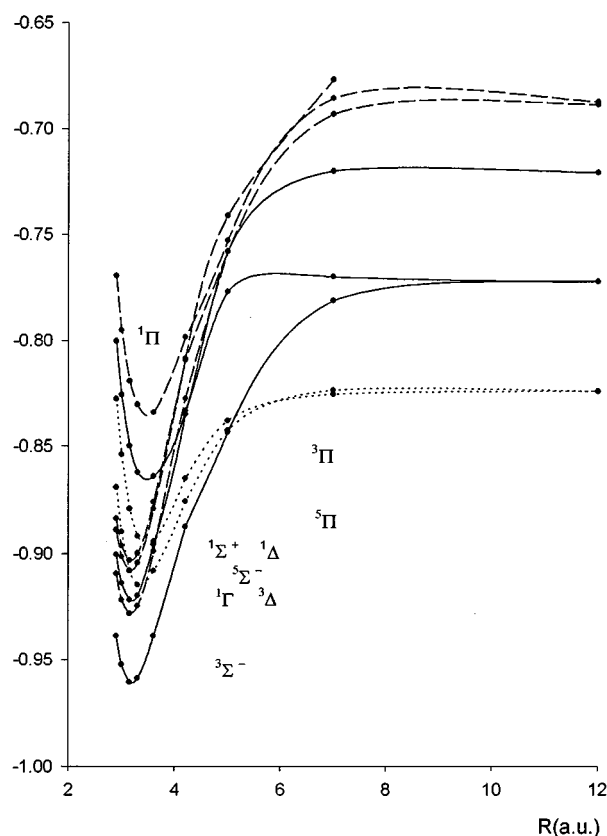


FIG. 1. Potential energy curves of nine low-lying electronic states of the MoC molecule as derived from CASSCF calculations.

electron Darwin contact term and for the relativistic correction due to the mass-velocity term. Since the states $^1\Sigma^+$ and $^1\Gamma$ arise from almost identical configurations, the relativistic corrections are assumed identical for these states.

The CASSCF calculations have been performed as functions of the internuclear distance, i.e., for the distances 2.9, 3.0, 3.15, 3.3, 3.6, 4.2, 5.0, 7.0, and 12.0 a.u. for the states $^1\Pi$, $^1\Delta$, $^3\Sigma^-$, $^3\Pi$, $^3\Delta$, $^5\Sigma^-$, and $^5\Pi$. For the states $^1\Sigma^+$ and $^1\Gamma$ the calculations have been performed for the internuclear distances 2.9, 3.0, 3.15, 3.3, 3.6, 4.2, and 5.0 a.u. Figure 1 shows the resulting potential energy curves based on potential energies that do not include the relativistic corrections. Figure 2 shows the potential energy curves obtained when the relativistic corrections have been included. Table I presents the spectroscopic constants obtained by solving the Schrödinger equation for the nuclear motion numerically using the potential energies derived in the CASSCF calculations excluding and including the relativistic corrections, respectively. The dissociation energies reported in Table I have been derived by subtracting the total energy at the equilibrium distance from the total energy of each state at 12 a.u., where available.

From Figs. 1 and 2, and also from Table I it is recognized that the electronic ground state of the MoC molecule is predicted to be $^3\Sigma^-$. Without considering the relativistic corrections the $^3\Sigma^-$ ground state is separated from the higher

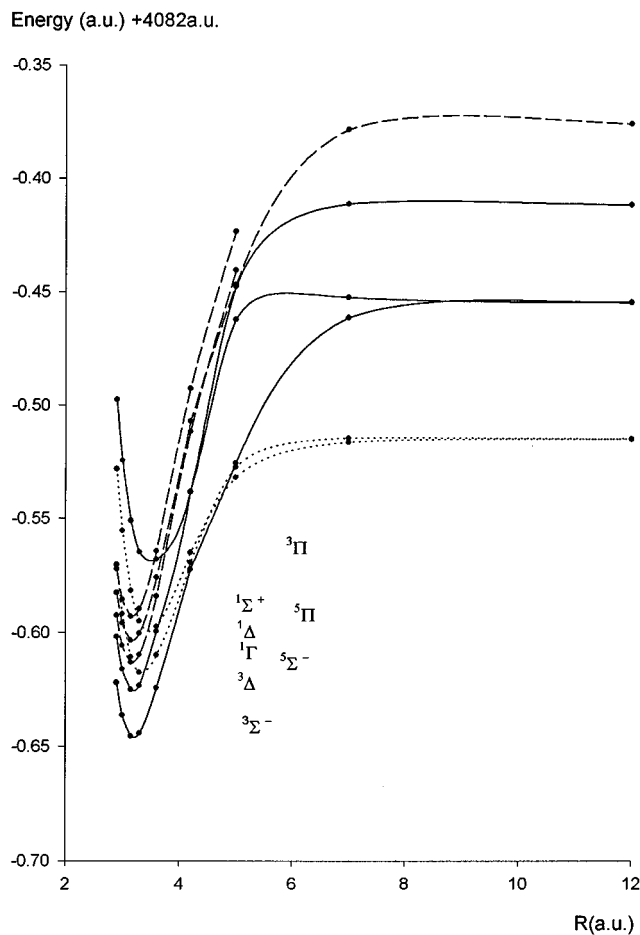


FIG. 2. Potential energy curves of eight low-lying electronic states of the MoC molecule as derived from CASSCF calculations including the relativistic corrections for the one electron Darwin contact term and for mass-velocity term.

lying states, $^1\Gamma$, $^3\Delta$, $^5\Sigma^-$, $^1\Sigma^+$, $^1\Delta$, $^5\Pi$, $^3\Pi$, and $^1\Pi$, by the calculated transition energies 7147, 8516, 10067, 11580, 12642, 14201, 20 878, 27 565 cm^{-1} , respectively. It is noted that the relativistic corrections cause the energy splittings between some of the low-lying states to decrease significantly resulting in interchanges of some of the low-lying

electronic states. Thus, the lowest lying excited state not considering the relativistic corrections is $^1\Gamma$, while the relativistic corrections cause the states $^3\Delta$ and $^5\Sigma^-$ states to drop below the $^1\Gamma$ state. The resulting energy separation between the $^3\Sigma^-$ ground state and the states $^3\Delta$, $^5\Sigma^-$, and $^1\Gamma$ are 4500, 6178, and 7207 cm^{-1} , respectively. By comparing Figs. 1 and 2 with Table I it is noted that the states having the largest relativistic corrections are those having the largest occupation of the Mo 5s orbital.

The relativistic corrections vary with the internuclear distances. From Table I it is noted that the relativistic correction cause the dissociation energies to increase. The positive charge associated with the Mo atom presumably causes the relativistic corrections to be larger at distances close to the equilibrium distance than at distances close to the dissociation limit. Furthermore, the relativistic corrections causes the equilibrium distances in the singlet and triplet states to increase by approximately 0.005 Å, while the equilibrium distances decreases slightly in the quintet states. The vibrational frequencies for all the states, except the $^3\Pi$ state, are increased by between 7 and 32 cm^{-1} .

Spin-orbit coupling will cause splittings of states, and also mixing of states with identical Ω values. The mixing is especially important, when the states cross each other. At internuclear distances less than 4 a.u. the $^3\Sigma^-$ ground state is well separated from the higher lying states. Therefore, at the equilibrium internuclear distance the major effect of the spin-orbit coupling on the $^3\Sigma^-$ ground state is to split the state into two states with $\Omega=0$ and $\Omega=1$. However, at approximately 5 a.u. the $^3\Sigma^-$ state crosses the states $^5\Sigma^-$ and $^5\Pi$. Therefore, the lowest lying state with $\Omega=0$ will be mostly $^3\Sigma^-$ at the equilibrium internuclear distance, while it will be mostly $^5\Sigma^-$ at the dissociation limit. Likewise, the lowest lying state with $\Omega=1$ will be mostly $^3\Sigma^-$ at the equilibrium distance, and a mixture of primarily $^5\Sigma^-$ and $^5\Pi$ at the dissociation limit. The lowest lying state with $\Omega=2$ will resemble $^3\Delta$ at small internuclear distances, but at the dissociation limit it will be a mixture of the states $^5\Sigma^-$ and $^5\Pi$. The spin-orbit coupling will not cause significant changes of the spectroscopic constants for the $^3\Sigma^-$ ground state as presented in Table I, but there will be changes for the

TABLE I. Spectroscopic constants of the low-lying electronic states of the MoC molecule as derived from the results of CASSCF calculations.

State	Without relativistic corrections					With relativistic corrections			
	Equilibrium distance, r_e (Å)	Vibrational frequency, ω_e (cm^{-1})	Transition energy, T_e (cm^{-1})	Dissociation energy, ^a D_e (eV)	Population of Mo 5s at 3.15 a.u.	Equilibrium distance, r_e (Å)	Vibrational frequency, ω_e (cm^{-1})	Transition energy, T_e (cm^{-1})	Dissociation energy, ^a D_e (eV)
$^3\Sigma^-$	1.688	962	0	5.13	0.20	1.693	971	0	5.20
$^1\Gamma$	1.670	1035	7147		0.18	1.675	1042	7207	
$^3\Delta$	1.688	983	8516	5.48	0.80	1.692	1013	4500	5.81
$^5\Sigma^-$	1.771	859	10067	2.48	0.76	1.769	891	6178	2.80
$^1\Sigma^+$	1.671	1025	11580			1.676	1032	11639	
$^1\Delta$	1.674	1012	12642	5.84	0.84	1.678	1026	9312	6.19
$^5\Pi$	1.837	783	14201	1.97	0.80	1.836	807	10228	2.30
$^3\Pi$	1.831	751	20878	2.55	0.77	1.838	721	16864	3.12
$^1\Pi$	1.852	770	27565	4.02					

^aDerived as the difference between the total molecular energy at the equilibrium distance and at the internuclear distance 12 a.u. for each state.

states, where crossings occur close to equilibrium internuclear distances.

The MoC molecule is polar. In all the low-lying states there is charge transfer from the Mo to the C atom resulting in positive gross atomic charges on Mo of $0.25e$, $0.24e$, $0.30e$, $0.28e$, $0.28e$, $0.27e$, and $0.30e$ at 3.15 a.u. in the states $^3\Sigma^-$, $^1\Gamma$, $^3\Delta$, $^5\Sigma^-$, $^1\Delta$, $^5\Pi$, and $^3\Pi$, respectively. The calculated dipole moment obtained amounts to 6.15, 6.14, 2.16, and 1.44 D, for the states $^3\Sigma^-$, $^1\Gamma$, $^3\Delta$ and $^1\Delta$ at 3.15 a.u., which is close to the equilibrium internuclear distances for these states. At the internuclear distance 3.3 a.u. the dipole moments of the states $^5\Sigma^-$, $^5\Pi$, and $^3\Pi$, amount to 1.73, 2.06, and 1.54 D.

IV. MRCI CALCULATIONS ON THE $^3\Sigma^-$ GROUND STATE AND THE $^3\Pi$ EXCITED STATE

In the CASSCF calculations reported above, the populations of the two lowest lying valence σ orbitals, 11σ and 12σ , are close to two at internuclear distances close to the equilibrium distance of the molecule. These findings have been utilized to determine molecular orbitals appropriate for use in the MRCI calculations. The molecular orbitals used in the MRCI calculations have been optimized in CASSCF calculations where the 11σ and 12σ orbitals were kept fully occupied. The 11σ orbital is essentially the C $2s$ orbital, and the 12σ orbital is the bonding σ orbital composed of the C $2p\sigma$ and the Mo $4d\sigma$. The reference configurations used in the MRCI calculations were required to have two electrons in the 2δ orbitals, and the orbitals 11σ and 12σ were kept fully occupied. This resulted in 37, respectively 36, reference configurations for the states $^3\Sigma^-$ and $^3\Pi$. All single and double excitations from the valence orbitals of the reference configurations have been included in the MRCI calculations. This resulted in a total of 507 055 configurations for $^3\Sigma^-$ and 508 231 configurations for $^3\Pi$ in the final MRCI calculations.

The MRCI calculations have been performed for the internuclear distances 2.9, 3.0, 3.15, 3.3, and 3.6 a.u. However, to get an improved description of the potential around the equilibrium distance for the $^3\Pi$ state MRCI calculations have also been performed at 3.45 and 3.8 a.u. for this state.

For the $^3\Sigma^-$ ground state the contribution of the major configuration, $(10\sigma)^2(11\sigma)^2(5\pi)^4(2\delta)^2$, amounts to 84% when derived in the CASSCF calculations, and to 80% when derived in the MRCI calculations at 3.15 a.u. Furthermore, all the configurations that have coefficients numerically larger than 0.05 in the MRCI calculations are all included in the CASSCF calculations. The gross atomic charge on Mo amounts to $0.29e$ and the dipole moment to 6.15 D at 3.15 a.u. For the $^3\Pi$ state the contribution of the major configuration, $(10\sigma)^2(11\sigma)^2(12\sigma)^1(5\pi)^3(2\delta)^2$, amounts to 81% when derived in MRCI calculations at 3.45 a.u. At 3.45 a.u. the gross atomic charge on Mo amounts to $0.31e$ and the dipole moment to 2.74 D in the $^3\Pi$ state.

The spectroscopic constants have been obtained by solving the Schrödinger equation for the nuclear motion numerically. Using the potential energies for the $^3\Sigma^-$ ground state

derived in the MRCI calculations without the relativistic corrections gives, $\omega_e = 990 \text{ cm}^{-1}$ and $r_e = 1.683 \text{ Å}$. When the relativistic corrections are included $\omega_e = 997 \text{ cm}^{-1}$ and $r_e = 1.688 \text{ Å}$. Correspondingly, the spectroscopic constants for the $^3\Pi$ state without the relativistic corrections are derived as, $\omega_e = 844 \text{ cm}^{-1}$ and $r_e = 1.807 \text{ Å}$. When the relativistic corrections are included $\omega_e = 848 \text{ cm}^{-1}$ and $r_e = 1.819 \text{ Å}$. The transition energy between the $^3\Sigma^-$ ground state and the $^3\Pi$ state is $20\,050 \text{ cm}^{-1}$ without considering the relativistic corrections. The relativistic corrections cause the transition energy to reduce to $15\,484 \text{ cm}^{-1}$.

It is noted that the equilibrium distance for the $^3\Sigma^-$ ground state derived in the MRCI calculations including the relativistic corrections is identical to that derived in the CASSCF calculations. The changes that occurs in the $^3\Pi$ state when performing MRCI relative to CASSCF calculations are not only due to the change of calculational method, but also to the inclusion of the additional points. Altogether the MRCI calculations do not result in major changes as compared to the results of the CASSCF calculations. Therefore, the discussion of the low-lying electronic states in Sec. VI is based on the results obtained in the CASSCF calculations described in Sec. III.

V. THE DISSOCIATION ENERGY OF MoC

The experimental value of the dissociation energy for MoC from the mass spectroscopic equilibrium measurements¹⁰ has been re-evaluated using the values of r_e and ω_e obtained in the MRCI calculations combined with the transition energies obtained in the CASSCF calculations, both including the relativistic corrections. The values for the revised Gibbs energy functions, $-(G_T^0 - H_0^0)/T$, in $\text{J K}^{-1} \text{ mol}^{-1}$ and enthalpy increments, $H_T - H_0$, in kJ mol^{-1} , are for: 298.15 K, 205.0 and 8.774; 2200 K, 270.4 and 84.90; 2400 K, 273.8 and 94.70; 2600 K, 277.0 and 104.7; 2800 K, 280.0 and 114.7; 3000 K, 282.8 and 124.8; 3200 K, 285.5 and 134.9. With these values the third law enthalpy for the reaction $\text{Mo(g)} + \text{C(graph.)} = \text{MoC(g)}$ becomes 228.2 ± 2.7 (S.D.) or $228 \pm 13 \text{ kJ mol}^{-1}$, when all errors are considered. The dissociation energy, D_0^0 of MoC becomes $483 \pm 13 \text{ kJ mol}^{-1}$ or $5.01 \pm 0.13 \text{ eV}$.

The $^3\Sigma^-$ ground state does not dissociate into the 7S_g ground term of the Mo atom, but rather into the 5S_g term. As reported in Table I, the adiabatic dissociation energy, D_e of the $^3\Sigma^-$ ground state of the MoC molecule has been derived as 5.13 eV without relativistic correction and as 5.20 eV including the relativistic corrections. Taking into account the zero-point vibrational energy, the corresponding values of D_0^0 amount to 5.07 eV, respectively 5.14 eV. However, it is the diabatic value of the dissociation energy that should be compared to the experimental value of $5.01 \pm 0.13 \text{ eV}$. The state $^5\Sigma^-$ dissociates into ground term atoms, and therefore an approximate value for the diabatic dissociation energy has been obtained by subtracting the transition energy of the $^5\Sigma^-$ state at 12 a.u. from the adiabatic value of the dissociation energy. Thus, the diabatic value of the dissociation energy, D_0^0 is derived as 3.66 and 3.50 eV, excluding and in-

TABLE II. The contributions of the major configurations to the CASSCF wave functions describing the $^3\Sigma^-$ ground state and the low-lying excited states, $^1\Gamma$, $^3\Delta$, $^5\Sigma^-$, $^1\Sigma^+$, $^1\Delta$, $^5\Pi$, $^3\Pi$, and $^1\Pi$ of the MoC molecule as functions of the internuclear distance.

State	Valence shell configuration							Contribution of valence shell configuration (%)					
								Internuclear distance (a.u.)					
	10σ	11σ	12σ	13σ	5π	6π	2δ	2.9	3.0	3.15	3.3	3.6	4.2
³ Σ [−]	2	2	0	0	4	0	2	89	87	84	81	70	35
¹ Γ	2	2	0	0	4	0	2	91	90	88	87	82	70
³ Δ	2	2	1	0	4	0	1	91	89	87	85	78	57
⁵ Σ [−]	2	1	1	0	4	0	2	90	89	86	83	73	33
¹ Σ ⁺	2	2	0	0	4	0	2	90	89	88	86	81	68
¹ Δ	2	2	1	0	4	0	1	91	90	88	85	79	58
⁵ Π	2	2	1	0	3	0	2	92	91	89	87	82	65
³ Π	2	2	1	0	3	0	2	91	90	88	85	79	57
¹ Π	2	2	1	0	3	0	2	89	87	84	81	77	58

cluding relativistic corrections, respectively. Thus, the calculated dissociation energy accounts for 73% or 70% of the experimental value, excluding or including relativistic corrections, respectively.

VI. THE LOW-LYING ELECTRONIC STATES OF MoC

Table II shows the contributions of the major configurations in the CASSCF wave functions for the electronic ground state, $^3\Sigma^-$, and for the low-lying excited electronic states as functions of the internuclear distance.

From Table II it is recognized that the low-lying electronic states of the MoC molecule at the respective equilibrium distances essentially arise from the following configurations: $(10\sigma)^2(11\sigma)^2(5\pi)^4(2\delta)^2$, for the states $^3\Sigma^-$, $^1\Gamma$, $^1\Sigma^+$, $(10\sigma)^2(11\sigma)^2(12\sigma)^1(5\pi)^4(2\delta)^1$, for the states $^3\Delta$ and $^1\Delta$, and $(10\sigma)^2(11\sigma)^2(12\sigma)^1(5\pi)^3(2\delta)^2$, for the Π states, i.e., $^5\Pi$, $^3\Pi$, $^1\Pi$. The $^5\Sigma^-$ state has the configuration $(10\sigma)^2(11\sigma)^1(12\sigma)^1(5\pi)^4(2\delta)^2$. Except for the configurations $(10\sigma)^2(11\sigma)^2(12\sigma)^1(5\pi)^4(2\delta)^1$ the above mentioned configurations are those expected when the Mo $(4d\sigma)^1(4d\pi)^2(4d\delta)^2(5s)^1$ interacts with the C atom in either of the configurations $(2p\pi)^2$ or $(2p\sigma)^1(2p\pi)^1$. The configuration $(10\sigma)^2(11\sigma)^2(12\sigma)^1(5\pi)^4(2\delta)^1$ can be considered as arising when an electron in the nonbonding 2δ orbitals in the configuration $(10\sigma)^2(11\sigma)^2(12\sigma)^1(5\pi)^3(2\delta)^2$ is transferred into the bonding 5π orbitals. This is expected to strengthen the chemical bond, and it is consistent with the findings that both states, $^3\Delta$ and $^1\Delta$, have lower energies than the lowest lying state of Π symmetry, $^5\Pi$.

Figures 3 and 4 present the populations of the individual atomic orbitals of Mo and C as functions of the internuclear distance for the $^3\Sigma^-$ ground state and for the lowest lying excited state, $^3\Delta$.

Figure 3 shows that the interaction resulting in a MoC molecule in the $^3\Sigma^-$ ground state is due to Mo $(4d\sigma)^1(4d\pi)^2(4d\delta)^2(5s)^1$ and C $(2s)^2(2p\sigma)^1(2p\pi)^1$. As the atoms approach each other the configuration of the C atom changes to $(2s)^2(2p\pi)^2$, and charge is transferred from the Mo $5s$ into the C $2p\sigma$ orbital resulting in a gross

atomic charge of $0.59e$ on C at 5.0 a.u. As the internuclear distance is further decreased, bonding molecular orbitals are formed between the C $2p\pi$ and Mo $4d\pi$ as well as in between the C $2p\sigma$ and the Mo $4d\sigma$. This results in the formation of the triple bond in the $^3\Sigma^-$ ground state. Formally

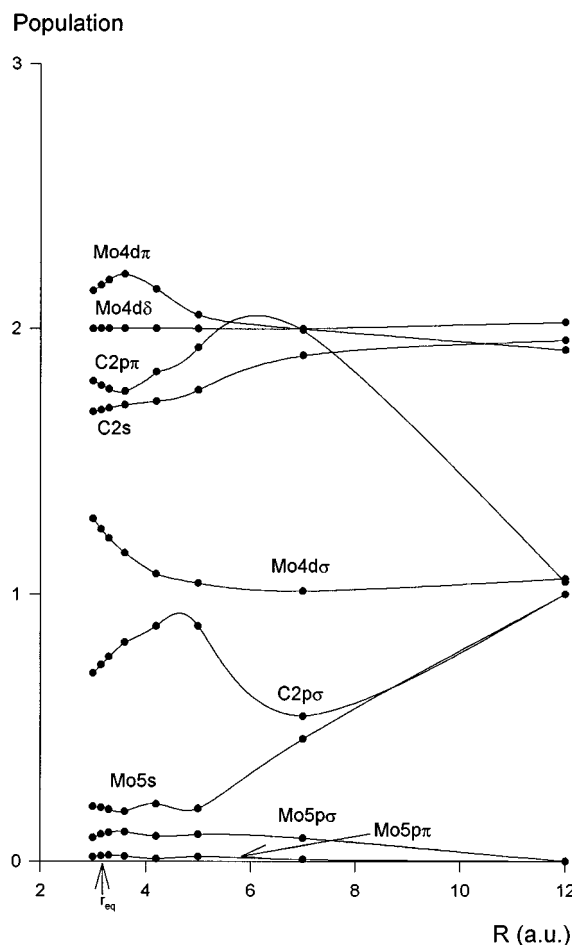


FIG. 3. Populations associated with the valence orbitals of the atoms Mo and C in the $^3\Sigma^-$ electronic ground state of MoC as derived from CASSCF wave functions. The equilibrium distance of the state is indicated by r_{eq} .

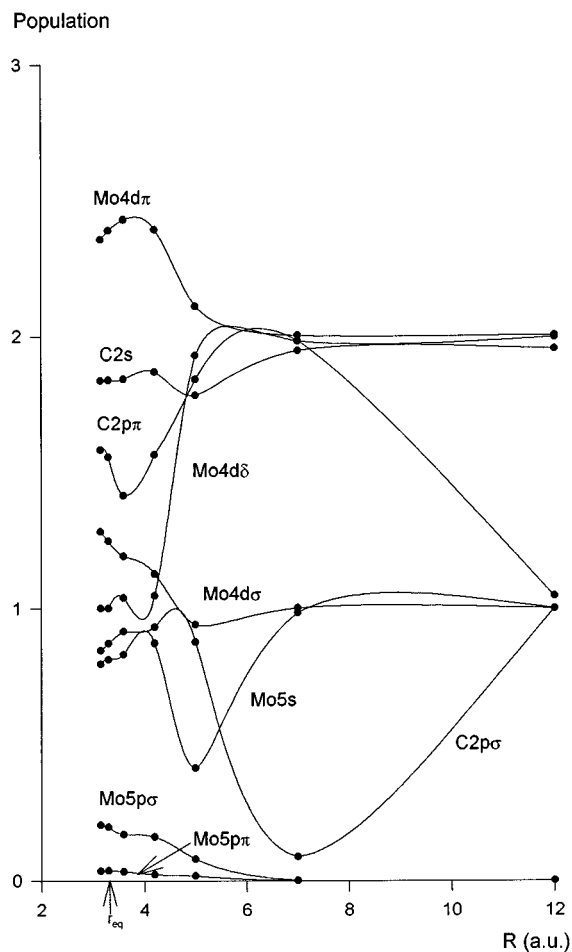


FIG. 4. Populations associated with the valence orbitals of the atoms Mo and C in the $^3\Delta$ low-lying electronic state of MoC as derived from CASSCF wave functions. The equilibrium distance of the state is indicated by r_{eq} .

the configuration $(10\sigma)^2(11\sigma)^2(5\pi)^4(2\delta)^2$ accounts for a quadruple bond between the atoms Mo and C, but it is noted from Fig. 3 that the population of the C $2s$ orbital is quite close to two, and therefore, this orbital cannot be appreciably bonding. The chemical bond in the $^3\Sigma^-$ ground state of the MoC molecule should thus be described as a triple bond due to the formation one bonding σ and two bonding π orbitals, which are approximately fully occupied at the equilibrium internuclear distance.

In the $^3\Delta$ state, Fig. 4, the interaction also occurs between the Mo $(4d\sigma)^1(4d\pi)^2(4d\delta)^2(5s)^1$ and C $(2s)^2(2p\sigma)^1(2p\pi)^1$. At internuclear distances between 12 and 7 a.u. the configuration of the C atom changes to $(2s)^2(2p\pi)^2$. As the internuclear distance is decreased to 5 a.u. charge is transferred especially from the Mo $5s$ orbital into the C $2p\sigma$ resulting in a gross atomic charge of $0.50e$ on C at 5 a.u. However, significant changes of the configuration occur as the internuclear distance is decreased from 5 to 4.2 a.u. The population of the Mo $4d\delta$ orbitals is decreased from approximately 2 to approximately 1, and the population of the Mo $5s$ orbital is increased. The chemical bond in the $^3\Delta$ state is a triple bond consisting of two π

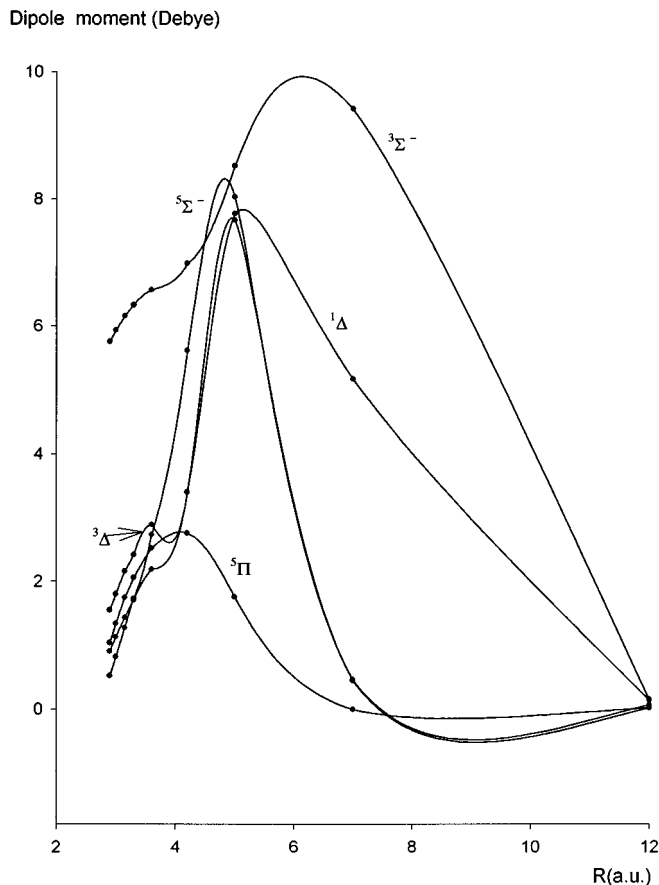


FIG. 5. Dipole moments of the $^3\Sigma^-$ ground state and of four excited electronic states, $^3\Delta$, $^5\Sigma^-$, $^1\Delta$, and $^5\Pi$, of the MoC molecule as derived from CASSCF wave functions.

bonds and one σ bond. The singly occupied σ orbital is essentially the nonbonding Mo $5s$ orbital.

Considering the results presented in Table II it is not surprising that the HF calculations are not sufficient to describe the electronic wave functions of MoC. It is noted that the major configuration $(10\sigma)^2(11\sigma)^2(5\pi)^4(2\delta)^2$ contributes less than 90% to the wave function of the $^3\Sigma^-$ ground state at internuclear distances close to the equilibrium distance. Similar trends are recognized for the other low-lying states. The remaining weights are distributed among many configurations. Thus, the wave functions for the low-lying states of the MoC molecule are truly multi configurational.

Figure 5 shows the dipole moments of the $^3\Sigma^-$ electronic ground state and of four low-lying electronic states of MoC, $^3\Delta$, $^5\Sigma^-$, $^1\Delta$, and $^5\Pi$ as derived from the CASSCF wave functions and as functions of the internuclear distances. It is noted that the dipole moments for all the states considered are very sensitive functions of the internuclear distances. The states $^3\Sigma^-$ and $^1\Gamma$ have much larger dipole moments than the remaining states. This is presumably connected to the population of the $5s$ orbital of Mo, since this orbital is part of a sp -hybrid that is polarized away from the internuclear region. At the internuclear distance 3.15 a.u. Table I shows that the population of the $5s$ orbital of Mo is

0.18e and 0.20e in the states $^3\Sigma^-$ and $^1\Gamma$, while it is in the range 0.76e–0.84e in the states $^3\Delta$, $^5\Sigma^-$, $^1\Delta$, $^3\Pi$, and $^5\Pi$.

The sequence of the low-lying electronic states of the MoC molecule is consistent with a qualitative molecular orbital diagram. In this diagram the lowest lying valence orbital, 10σ , is essentially the nonbonding C $2s$ orbital, and this orbital is practically doubly occupied in all the states investigated. The next higher lying orbitals are the bonding 5π and 11σ orbitals. Thereafter follows the nonbonding 2δ orbitals, Mo $4d\delta$. Higher in energy are the nonbonding 12σ orbital and the anti-bonding 6π orbitals. The molecular orbital diagram described here is in agreement with our previous results regarding the carbides PdC, RhC, and RuC.¹⁵

The $^3\Sigma^-$ ground state and the low-lying states $^1\Gamma$ and $^1\Sigma^+$, all with the approximate configuration $(10\sigma)^2(11\sigma)^2(5\pi)^4(2\delta)^2$, represent different couplings of the spin and space angular momenta. The states, $^3\Delta$ and $^1\Delta$, arise from the $^3\Sigma^-$ ground state by exciting one of the 2δ electrons into the 12σ orbital. In the states $^3\Delta$ and $^1\Delta$ the spins of the electrons in the singly occupied σ and δ orbitals are coupled parallel and anti parallel, respectively. Correspondingly, the Π states arise from the $^3\Sigma^-$ ground state when one 5π electron is excited into the 12σ orbital. Likewise, the $^5\Sigma^-$ state arises from the $^3\Sigma^-$ ground state by exciting one electron from the 11σ into the 12σ orbital.

VII. COMPARISON WITH OTHER TRANSITION METAL CARBIDES

The chemical bond and the low-lying electronic states of the MoC molecule described above are consistent with our findings for other carbides of the second transition metal series, especially RuC⁴ and RhC.² Thus, the low-lying states of the MoC molecule can be explained in terms of a molecular orbital diagram that is identical to that of RuC and RhC. The π orbitals are the main bonding orbitals, the excess of electrons in bonding relative to antibonding π orbitals amounts to 3.68e for MoC, 3.59e for RuC and 3.58e for RhC. For the electronic ground state of each molecule, the CI wave function exhibits a leading configuration consistent with the above mentioned orbital diagram. Thus, the leading configuration for the $^3\Sigma^-$ ground state of MoC is $(10\sigma)^2(11\sigma)^2(5\pi)^4(2\delta)^2$, while it is $(10\sigma)^2(11\sigma)^2(12\sigma)^1(5\pi)^4(2\delta)^3$ for the $^3\Delta$ ground state of RuC, and $(10\sigma)^2(11\sigma)^2(12\sigma)^1(5\pi)^4(2\delta)^4$ for the $^2\Sigma^+$ ground state of RhC. The chemical bonds in all three molecules are similar. They all have triple bond character, since the additional electrons in the molecules RuC and RhC relative to MoC occupy nonbonding orbitals.

The CrC molecule is isovalent with the MoC molecule, but the chemical bonds of the two molecules are of completely different nature.⁹ In the CASSCF wave function of CrC the leading configuration has a weight of less than 20% at the equilibrium internuclear distance of the molecule. This indicates that the $3d$ electrons of Cr are localized. The excess of electrons in bonding relative to antibonding π orbitals amounts to only 1.26e for CrC. The chemical bond in

CrC is due to the formation of a bonding σ orbital, but in addition, the localized π orbitals on the Cr and C atoms are valence bond coupled, and likewise there is valence bond coupling between the C $2p\sigma$ orbital and a $4s,4p$ hybrid orbital of Cr that is polarized away from the C atom. The four lowest lying electronic states of the CrC molecule are those expected, when the angular momenta of the ions 6S_g Cr⁺ and 4S_u C⁻ are coupled.

VIII. CONCLUSIONS

In the present work we have reported the results of the theoretical investigations performed for the MoC molecule. The electronic structure and the nature of the chemical bond in the MoC molecule have been elucidated by performing all electron *ab initio* MCSCF (CASSCF) and MRCI calculations.

The electronic ground state of the MoC molecule has been predicted as being $^3\Sigma^-$ with the approximate orbital configuration $(10\sigma)^2(11\sigma)^2(5\pi)^4(2\delta)^2$. Based on the results obtained in the MRCI calculations including the relativistic corrections, the spectroscopic constants of the MoC molecule in the $^3\Sigma^-$ ground state have been determined as $r_e = 1.688$ Å and $\omega_e = 997$ cm⁻¹. According to the results obtained in the CASSCF calculations including the relativistic corrections the $^3\Sigma^-$ ground state is separated from the next higher lying states, $^3\Delta$, $^5\Sigma^-$, $^1\Gamma$, $^1\Delta$, $^5\Pi$, $^1\Sigma^+$, and $^3\Pi$ by 4500, 6178, 7207, 9312, 10 228, 11 639, and 16 864 cm⁻¹, respectively. The transition energy between the $^3\Sigma^-$ ground state and the $^3\Pi$ excited state is reduced to 15 484 cm⁻¹ in the MRCI calculations including the relativistic corrections.

The chemical bond in the $^3\Sigma^-$ ground state of the MoC molecule has triple bond character due to the formation of one bonding σ and two bonding π molecular orbitals that are approximately fully occupied at the equilibrium internuclear distance.

The sequence of the low-lying electronic states of the MoC molecule are in accordance with a molecular orbital diagram, where the lowest lying valence orbitals in energy sequence are: 10σ , 5π , 11σ , and 2δ . Thereafter follow the orbitals 12σ and 6π . These latter orbitals are empty in the $^3\Sigma^-$ ground state.

The dissociation energy, D_0 of the $^3\Sigma^-$ ground state of MoC derived in the CASSCF calculations including the relativistic corrections and corrected for zero-point vibrational energy amounts to 3.50 eV. This is 70% of the experimental value of 5.01 eV.

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